# <International Research Center for Elements Science>Organometallic Chemistry

# International Research Center for Elements Science – Organometallic Chemistry –

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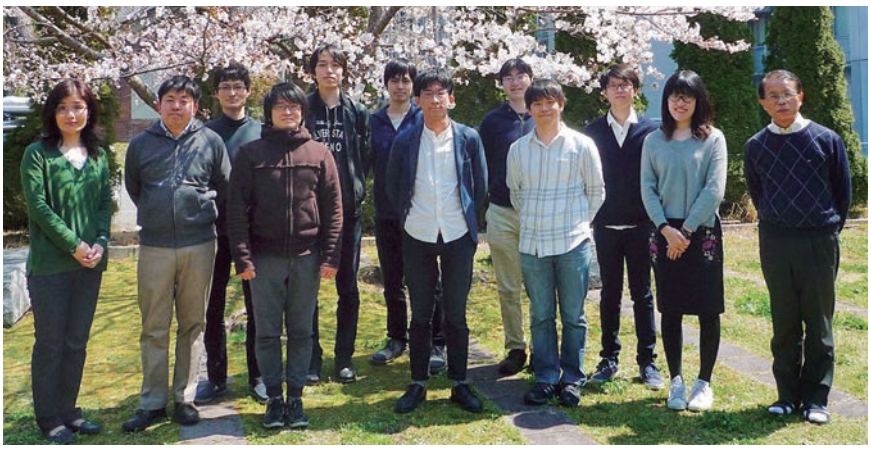
## Scope of Research

This laboratory aims to establish new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using experimental methods such as spectroscopy and kinetic techniques, as well as theoretical methods. The research subjects include: 1) development of novel organotransition metal systems for catalysis based on precise ligand design, and 2) preparation of π-conjugated polymers using direct arylation.

### KEYWORDS

Transition Metal Complex
Homogeneous Catalyst
Reaction Mechanism
Low-coordinate Phosphorus Ligand
π-Conjugated Polymer



## Selected Publication

Wakioka, M.; Takahashi, R.; Ichihara, N.; Ozawa, F., Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Highly Selective Synthesis of π-Conjugated Polymers with Diketopyrrolopyrrole Units, *Macromolecules*, **50,** 927-934 (2017).

## A Square Planar Complex of Platinum(0)

The Pt(0) complex [Pt(PPh$_3$)(Eind$_2$-BPEP)] with a pyridine-based PNP-pincer-type phosphaalkene ligand (Eind$_2$-BPEP) has a highly planar geometry around Pt with Σ(Pt) = 358.6°. This coordination geometry is very uncommon for formal d$^{10}$ complexes, and the Pd and Ni homologues with the same ligands adopt distorted tetrahedral geometries. DFT calculations reveal that both the Pt and Pd complexes are M(0) species with nearly ten valence electrons on the metals whereas their atomic orbital occupancies are evidently different from one another. The Pt complex has a higher occupancy of the atomic 6s orbital because of strong s–d hybridization due to relativistic effects, thereby adopting a highly planar geometry reflecting the shape and orientation of the partially unoccupied $d_{x2-y2}$ orbital.

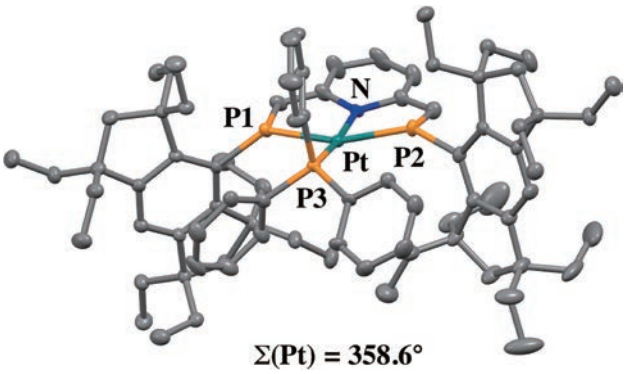



**Figure 1.** Molecular Structure of [Pt(PPh$_3$)(Eind$_2$-BPEP)].

## Square Planar Pt(0) Phosphaalkene Complexes

Recently, we found that the platinum(0) complex [Pt(PPh$_3$)(Eind$_2$-BPEP)] (**1**) coordinated with a pyridine-based PNP-pincer type phosphaalkene ligand (Eind$_2$-BPEP) adopts a highly planar structure around the platinum; this coordination geometry is very uncommon for four-coordinate complexes of formal d$^{10}$ metals. In this study, we synthesized [Pt(L)(Eind$_2$-BPEP)] type derivatives of **1** having a series of L [DMAP (**2**), 3,5-lutidine (**3**), PMe$_3$ (**4**), *t*BuNC (**5**), CO (**6**)], and examined the effects of L on the coordination geometry and spectroscopic properties. The X-ray analysis of **3**, **4**, and **6** demonstrated highly planar coordination geometry comparable to **1**. Complexes **2**–**6** displayed strong absorption in a near infrared region, exhibiting a very deep color in solution as well as in the solid. These absorption bands due to the HOMO–LUMO transitions tended to shift to a shorter wavelength as the π-accepting ability of L increased.

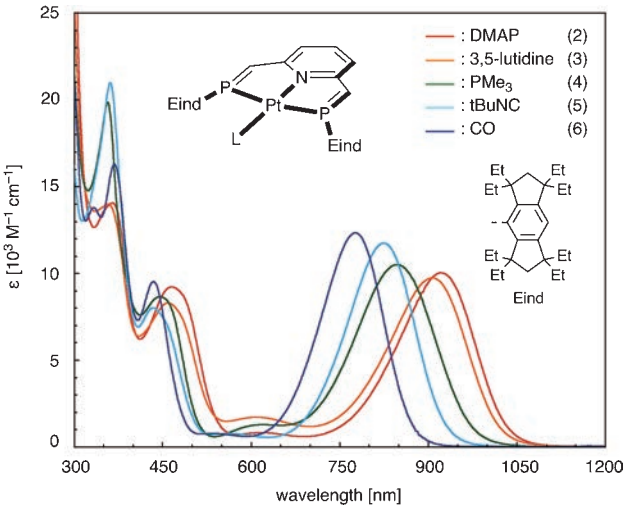
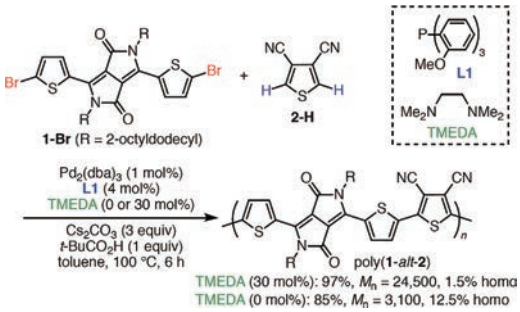



**Figure 2.** UV-vis-NIR spectra of [Pt(L)(Eind$_2$-BPEP)] complexes in THF at room temperature.

## Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Highly Selective Synthesis of π-Conjugated Polymers with Diketopyrrolopyrrole Units

We found that the combined use of P(2-MeOC$_6$H$_4$)$_3$ (**L1**) and TMEDA as ligands effectively prevents defect formation in palladium-catalyzed direct arylation polymerization (DArP) to give donor-acceptor polymers (DA polymers) with diketopyrrolopyrrole (DPP) units. The reaction of 3,6-bis(5-bromo-2-thienyl)diketopyrrolopyrrole (**1-Br**) and 3,4-dicyanothiophene (**2-H**) in the presence of **L1** as the only ligand formed a notable amount of insoluble materials via branching and cross-linking, and the soluble part ($M_n$ = 3100) contained a large quantity of homocoupling defects (12.5%). In contrast, in the presence of **L1** and TMEDA, the formation of insoluble materials was completely suppressed, and homocoupling defects decreased to 1.6%. Moreover, the molecular weight of poly(**1**-*alt*-**2**) remarkably increased ($M_n$ = 24500, 97% yield).




**Scheme 1.**